

Interactive comment on “Recent increases in the atmospheric growth rate and emissions of HFC-23 (CHF₃) and the link to HCFC-22 (CHClF₂) production” by Peter G. Simmonds et al.

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We thank the Referee #2 for their time and effort in evaluating this manuscript and for their suggestions for improvements. Our responses to the points made by the reviewer are addressed on the following pages. Replies to Referee 2 This manuscript reports an update of the evolution of global mole fractions and emissions of HFC-23, an important greenhouse gas. The findings are novel and interesting and the overall work is certainly of sufficient quality for publication in ACP. I would however suggest a) clarifying the reasons for publishing this gas separately from the 2017 Simmonds paper on HFCs and HCFCs and b) the following changes: Reply. The principal reason for a separate

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paper on HFC-23 is that unlike the other HFCs this is not a replacement fluorocarbon, but a compound with a more unique history as an unavoidable by-product of HFC-22 production. As such, we felt that it deserved a separate analysis, consistent with increasing attention and interest from the atmospheric science community.

L33-36 I'm not sure what the authors want to say here. Does this mean that the HCFC22 production process has been releasing an increasingly high fraction of HFC-23 or are other sources important, too? This should be clarified in a concise way. Reply. Here we are just reporting HCFC-22 mole fractions. The following sentence has been added to clarify.

This slowing growth is consistent with demand for HCFC-22 moving from dispersive to feedstock uses, but HFC-23 emissions are a consequence of incomplete mitigation from all HCFC-22 production.

L47-49 So which regions are likely to be responsible for the other 98.5 %? Reply. We have added the following sentences. The majority of the increase in global HFC-23 emissions is attributed to a delay in the adoption of mitigation technologies, predominately in China and East Asia. However, a reduction in emissions is anticipated, when the Kigali 2016 amendment to the Montreal Protocol requiring HCFC and HFC production facilities to introduce destruction of HFC-23 is fully implemented.

L53-58 This sentence is very long. Consider splitting it up to improve readability. L75 The date of that reference is inconsistent with the one in the reference list. Reply. Sentence has been split into two as requested. We also thank the referee for noting the reference error which has been corrected. Hydrofluorocarbons (HFCs) have been introduced as replacements for ozone-depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), for example, HFC-134a as a direct replacement for CFC-12. Conversely, HFC-23 is primarily an unavoidable by-product of chlorodifluoromethane HCFC-22 (CHClF₂) production due to the over-fluorination of chloroform (CHCl₃).

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L75-91 This section is a rather abrupt change from the previous and could benefit from short introductory sentence or sub-heading. I would also suggest moving to after the next paragraph. Reply. Introductory sentence has been added. There have been a significant number of previously published papers related to HFC-23. Oram et al., (2008).....etc... L88-91 I'm not sure why the extra details are relevant. Surprisingly, the reference to Simmonds et al., 2017, who reported HCFC-22 observations and emissions from the same network (and repeatedly discussed HFC-23), is missing, as are any other papers on HCFC-22. Reply. Extra details have been removed as requested. In addition we have moved lines 66-69 to a new paragraph (after line 90) and added the following text. We have previously reported on the changing trends and emissions of HCFC-22 (Simmonds et al. 2017) and references therein. L126-169 There are quite a lot of technical details in this section, which do not contribute to the main messages of the paper. These methods are also well established and I suggest moving large parts of the section to the supplement to improve readability. Reply. We have moved the bulk of the methodology in Section 2 to the supplementary material, leaving only a brief description as follows-: Ambient air measurements of HFC-23 and HCFC-22 at each site are recorded using the AGAGE GC-MS-Medusa instrument which employs an adsorbent-filled (HayeSep D) microtrap cooled to $\sim -175^{\circ}\text{C}$ to pre-concentrate the analytes during sample collection of 2litres of air (Miller et al., 2008; Arnold et al., 2012). Samples are analysed approximately every 2 hours and are bracketed by measurements of quaternary standards to correct for short-term drifts in instrument response. Additional details of the analytical methodology are provided in the Supplementary material.

L203 I would be interested to know the methodology used to calculate this "liberal estimate". Is there a reference and could more information specifically on HFC-23 and HCFC-22 be given in the supplement? Reply. As noted above this is a very subjective question, since we cannot really know something that we cannot measure. As we explain, we are nevertheless obliged to estimate absolute accuracy for modelling purposes and we have revised the paragraph in question in order to make these points

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more clearly. Estimates of absolute accuracy are nevertheless needed for interpretive modelling applications, so despite the subjective nature of the question it is incumbent on those responsible for the measurements to provide an assessment of accuracy. Accordingly, we liberally estimate the absolute accuracies of these measurements as -3% to +2% for HFC-23 and $\pm 1\%$ for HCFC-22. The larger and asymmetric uncertainty for HFC-23 is due to its lower atmospheric and standard concentration, and to the lower stated purity of the HFC-23 reagent used to prepare the primary calibration scale, respectively.

L277 The annual growth probably relates to all of 2016, not just the end of that year? Reply. Yes agreed and corrected L293-296 The authors should make it clear that they have already published the HCFC22 data they refer to here. Reply. Following text has been added. These results are an update of our previously reported analysis of HCFC-22 (Simmonds et al., 2017).

L314-316 It is not clear whether this agrees with Carpenter and Reimann (2014) or not. Reply. The text has been revised as follows: These HFC-23 emissions estimates are slightly lower in 2006 and slightly higher in 2009 than the HFC-23 estimates of Miller et al., (2010) and Carpenter and Reimann, (2014).

L469 Please correct: un-abated. Reply. Corrected. L779-781 As published in Simmonds et al., 2017? Reply. The following text has been added to the note for Table 3. These HCFC-22 global emissions estimates are updates for HCFC-22 emissions reported in Simmonds et al. (2017) L800-816 Missing from the two figures is previously published data and the respective sections of the manuscript would also benefit from a discussion of how mole fractions compare with published data. The axes on the inset of the first figure are very hard to read and the firm air is missing from the legend. Reply. These two figures have been modified for additional clarity and the font size on the inset in Figure 1 has been increased. We previously discussed mole fractions in Section 3.2 and there is only a limited amount of additional reported observations of HFC-23 mixing ratios. We have added the following text to the introduction to include

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references to these limited observations. Kim et al., (2010) reported HFC-23 measurements (November 2007-December 2008) at Jeju Island, Korea and also estimated regional atmospheric emissions. Most recently Fang et al., (2014, 2015) have provided top down estimates of HFC-23 emissions from China and East Asia and included observed HFC-23 mixing ratios at three stations Gosan, Korea, and Hateruma and Cape Ochi-ishi, Japan.

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